

**MEASUREMENT OF CARBONYL COMPOUNDS
IN THE
CENTRAL CALIFORNIA OZONE STUDY**

Final Report

Submitted to

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October 30 , 2002

TABLE OF CONTENT

<u>SECTION</u>	Page
1. INTRODUCTION	2
2. TECHNICAL APPROACH	2
2.1 Ground Sampling	2
2.2 Aircraft Sampling.....	2
2.3 Analysis	3
2.4 Quality Control	3
2.5 Precision and Accuracy	4
3. RESULTS AND DISCUSSION.....	5
4. REFERENCES.....	11

1. INTRODUCTION

AtmAA Inc. was under contract to the California Air Resources Board (CARB) to conduct the measurement of C1 to C7 carbonyl compounds in the Central California Ozone Study (CCOS) in the summer of 2002. Carbonyl measurement was conducted on Intensive Operating Period (IOP) days on the ground at seventeen stations operated by the local air pollution control districts, and contractors. The ground stations included eight S1 sites: Arvin, Angiola, Bodega Bay, Piedras Blancas, San Andreas, Sutter Buttes, Turlock, White Cloud; two S1' sites: San Leandro, San Jose 4th Street; four S2 sites: Bethyl Island, Pacheco Pass, Trimmer; and three R sites: Granite Bay, Parlier, and Sunol. Carbonyl aloft was conducted by the aircrafts operated by Sonoma Technology, Inc.(STI), and University of California, Davis (UCD), and Tennessee Valley Authority (TVA). AtmAA provided the sampling equipment and collection cartridges for the study.

2. TECHNICAL APPROACH

2.1 Ground Sampling

AtmAA-impregnated DNPH C18 Sep-Pak cartridges (Waters, Milford, MA) without O₃ denuder was used. All ground sites were collecting four samples at hour intervals of 0-3, 6-9, 13-16, and 17-20 plus a blank, duplicate, during each IOP. Tandem cartridges were also used to assess breakthrough at each site. All samplers were leak-checked and flow-calibrated before shipping to the site for installation. The site operator was trained before the study on how to operate the equipment and conduct sample collection using the DNPH cartridge. All samplers received a final calibration upon returning from the field.

When an IOP day was forecasted, the technician would install the cartridges into the samplers on the day before and sampling took place at the prescribed times. On consecutive IOP days, the technician would come in some time during the day to remove the exposed cartridges and replenished with fresh cartridges. Exposed cartridges were returned to the laboratory after each intensive period. They were stored in the freezer until analysis.

2.2 Aircraft Sampling

Upper air samples were collected from fixed wing aircrafts by either ramming air (STI and TVA) or a stainless steel diaphragm pump (UCD) through a Teflon inlet tube into pre-cleaned 50-liter Tedlar bags that had been doped with sufficient quantity of NO (~15ml of 1000 ppm) to react with any O₃ in the air sample. The samples were shielded from light and, upon returning to the base, transferred through C18-DNPH cartridges to capture the carbonyls. Exposed cartridges were kept in a refrigerator, and returned in a cooler to the laboratory where they were stored until selection for analysis was made.

2.3 Analysis

The samples were analyzed at the laboratory in batches of approximately 20 to 40. Each cartridge was eluted with 3 ml of acetonitrile into a graduated polyethylene tube with a screw cap. The exact volume was calibrated gravimetrically. An aliquot of the eluent was transferred into a 2-ml septum vial and injected with an autosampler into a high performance liquid chromatograph (Shimadzu LC-6) for separation and quantitation of the hydrazones (Fung and Grosjean 1981). The samples were analyzed for formaldehyde, acetaldehyde, acetone, propanal, benzaldehyde, o-tolualdehyde, and C4 to C6 aliphatic carbonyls grouped by carbon number. Complete speciation of C4 and greater aliphatic carbonyls was deemed not critical to the program's objectives, and thus represented cost savings to the program.

Hydrazone standard solutions were used for the calibration of the carbonyls. The calibration factor for total C4 was the average response factor of crotonaldehyde, methylethyl ketone, methacrolein, and butanal. Total C5, and C6 carbonyls were referenced to pentanal, and hexanal respectively. Since the DNPH chromophore is responsible for the UV absorption, calibration for total carbonyl using a ketone or aldehyde produces similar results.

The carbonyl concentrations, in ppb, were computed from the amounts measured after blank correction and the volume of air sampled using the following equation:

$$\text{ppb}_i = \frac{m_i - b_i}{f \times t} \times 1000 \times \frac{24.45}{MW_i} \quad (1)$$

where ppb_i = concentration in ppb of carbonyl species, i ,
 m_i = μg of i measured in the sample,
 b_i = average μg of i in the blank,
 t = sampling duration, in minutes,
 f = sampling flow rate, in liters/min,
 MW_i = molecular weight of i .

2.4 Quality Control

The sampling equipment was leak-tested and calibrated prior to the delivery to the field. A standard operating procedure was provided to the site operators for reference. Samplers were re-calibrated after the program to determine if any significant change in the flow rates had occurred. The average of the pre- and post-study flow rates were used to determine the sample volume. Flow rate variability has been well within the $\pm 5\%$ specification of the controller.

DNPH cartridges used for the study were prepared from a single batch of pre-purified DNPH (~99.9996%) reagent. The impregnating solution was analyzed for carbonyl background prior to using for the impregnation. Several finished cartridges were also analyzed to confirm that the carbonyl background was within acceptable limits. The cartridges were sealed by plugs and kept individually inside screw-capped vials to prevent contamination. Approximately 10 of these cartridges were packaged in sealed metal cans for storage in a refrigerator and shipment to the field via overnight delivery. A two-week supply of cartridges were shipped in coolers by next-day air to

the sites prior to the beginning of the study and were stored refrigerated until use. The remaining needs were filled by separate shipments to maintain an adequate supply, but also to ensure freshness of cartridges for low blank variability. Exposed cartridges were returned in a cooler chilled with blue ice at the conclusion of each intensive period.

Field blanks, duplicate samples, and tandem cartridges were collected in the study. Tandem cartridges were taken at the various time periods to assess breakthrough.

Quality control measures in the laboratory included instrument calibration for each batch of samples, replicates of standards, and approximately 10% of the samples for estimation of analytical precision.

2.5 Precision and Accuracy

The relative precision, $\frac{s_i}{C_i}$, of the carbonyl measurement can be estimated using the following equation (Watson et al, 1989) :

$$\left(\frac{s_i}{C_i} \right)^2 = \left[\frac{s_m^2 + s_b^2}{(m - b)^2} + \frac{s_v^2}{v^2} \right] \quad (2)$$

where

- s_i = standard deviation of carbonyl species C_i ,
- s_m = standard deviation of the mass of species i measured ,
- s_b = standard deviation of the mass of species i in the blank (i.e. blank variability),
- s_v = standard deviation of the sample volume v .

The analytical precision, s_m , can be approximated by the average of the standard deviation of each measured pair, m_{2i} and m_{1i} , of repeat sample analysis by (Watson et al):

$$s_m^2 = \frac{1}{2n} \sum_{i=1}^n (m_{2i} - m_{1i})^2 \quad (3)$$

and s_b determined from the standard deviation of the measured field blanks in the study. Sample volume is determined from flow rate and sampling duration. Since time is measured with very high precision by electronic timers, the error in the duration term is essentially zero. Thus, the precision of the volume measurement, s_v , can be estimated from the sampler flow deviations between the pre- and post-study sampler calibrations, f_1 and f_2 (EPA, 1984) or

$$\left(\frac{s_v}{v} \right)^2 \cong \left(\frac{s_f}{f} \right)^2 \cong \left\{ \left(\frac{f_2 - f_1}{1.128} \right) \times \frac{1}{f} \right\}^2 \quad (4)$$

The statistical parameters on flow, blank variability, and analytical precision are summarized in Table 1. The values of these parameters were inputted to Equation (2) to obtain the carbonyl

relative measurement precision, s_i / C_i , and are shown in Figures 1 and 2 over the concentration ranges of each carbonyl species measured.

There were duplicate (collocated) samples taken at all sites at the time period from 13-16 PDT through out the study. These duplicates are used to obtain measurement precision such as coefficient of variation (CV), which is the standard deviation relative to the mean of the population from which the standard deviation is derived. It is typically expressed in per cent basis. The CV can be estimated from the differences observed between duplicate measurements using the following equation (Youden 1977):

$$\begin{aligned} \text{CV (\%)} &= 100 \times \frac{s}{\mu} \\ &= 100 \times \sqrt{\frac{1}{n} \sum_{i=1}^n \frac{1}{u} (m_i - u)^2} \end{aligned} \quad (5)$$

where s = standard deviation,

μ = the mean of the population, (or pair, in this case)

m_i = i th observation in the population, and

n = number of pairs of observations

The CV's for the measurement of carbonyls have been calculated from collocated sample pairs from the study using Equation (5) and summarized along with other pertinent statistical parameters in Table 1.

3. RESULTS AND DISCUSSION

The complete set of the data was delivered electronically in CARB-specified format. It has been archived and validated with the VOC, meteorological and other data that were collected during the study.

Overall, the sampling equipment performed well through out the entire study. There were some loss of samples due to human error and unfamiliarity with the timer controlling the sampling. Sampler flow rates were maintained during the study as indicated in Table 1 by small differences observed between the pre- and post-study calibrations. Notable exception was Arvin which suffered from a large reduction of sampling flow due to a piece of styrofoam debris lodged into the sample line inlet. The data at Arvin was computed assuming the reduced sampling flow rate. The problems encountered at the various sites during the study are summarized in Table 2. Sites without any problem are omitted.

Field blanks and their variability were low, resulting in lower quantifiable limits (LQL) for 3-hour samples at approximately 0.4 ppbv or less for all compounds. The LQL at Arvin is expected to be 3 to 4 times higher due to the uncertainty in the flow rate. Likewise, the LQLs for the aircraft

samples are approximately 4.8 times higher due to the smaller sample volume. Analytical precisions (s_m) derived from repeat analysis are <0.02 ug for all compounds. The Coefficient of Variation derived from duplicate pairs of measurement ranged from of 3.7 to 7.8% for the compounds. (see Table 1). Precision estimates over the entire range of concentrations measured for each carbonyl species are graphically presented in Figure 1 and 2 to allow the uncertainty be assessed readily for all values in the data base. Aircraft samples have sample volumes typically about 5 times smaller than the ground samples, so their precision estimates would be correspondingly larger. To use the same plots to estimate the uncertainty in aircraft data, take the precision estimates at one fifth of the aircraft concentrations.

The tandem pairs of cartridges provided an assessment of the carbonyl collection efficiencies. The results indicated that breakthrough was not a problem for 3-hour samples. The collection efficiency of a carbonyl species, as defined by the ratio of the species amount measured in the upstream cartridge to the total amount in both up- and downstream cartridges, was calculated and shown in Table 1. In case a downstream value was negative, (i.e. sample value is lower than the blank) it was replaced by a zero for the calculation. All carbonyls showed a collection efficiency of $>90\%$ except for acetone ($\sim 88\%$) and benzaldehyde ($\sim 85\%$). Benzaldehyde was at very low concentrations, so the difference between the front and the back cartridge can easily be affected by the variation in the blank, making the break-through assessment not significant.

Table I: Summary of Statistical Parameters on Carbonyl Measurement in CCOS.

	HCHO	CH ₃ CHO	Acetone	Propanal	Benzal.	m-Tolual.	Sum C4	Sum C5	Sum C6
Blank									
Mean, ug	0.0533	0.0538	0.1599	0.0082	0.0277	0.0028	0.0673	0.0345	0.0183
Std Dev. (s _b)	0.0035	0.0045	0.0204	0.0021	0.0033	0.0014	0.0119	0.0085	0.0046
Count	49	49	49	49	49	49	49	49	49
3s _b	0.010	0.053	0.205	0.054	0.112	0.054	0.130	0.072	0.203
LQL at 3s _b , ppbv	0.063	0.220	0.644	0.171	0.193	0.082	0.330	0.153	0.370
Repeats:									
Std. Dev. (s _m), ug	0.0108	0.0104	0.0157	0.0050	0.0052	0.0048	0.0195	0.0140	0.0132
Count, pairs	107	107	107	107	107	107	107	107	107
Volume:									
Grd sites, m ³	0.134	0.134	0.134	0.134	0.134	0.134	0.134	0.134	0.134
Aircraft, m ³	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
Std Dev.(s _v), l/min	0.0187	0.0187	0.0187	0.0187	0.0187	0.0187	0.0187	0.0187	0.0187
s ² /V ² , average	0.00047	0.00047	0.00047	0.00047	0.00047	0.00047	0.00047	0.00047	0.00047
Coef. of Var, %	7.82	5.83	7.46	3.69	5.95	4.79	8.34	5.05	4.98
Mean conc., ppbv	4.49	2.29	3.05	0.52	0.07	0.09	1.56	1.02	0.81
Count, pairs	28	28	28	28	28	28	28	28	28
Collection Eff.,%	94.49	96.23	87.30	94.41	84.82	95.64	92.37	90.53	100.92

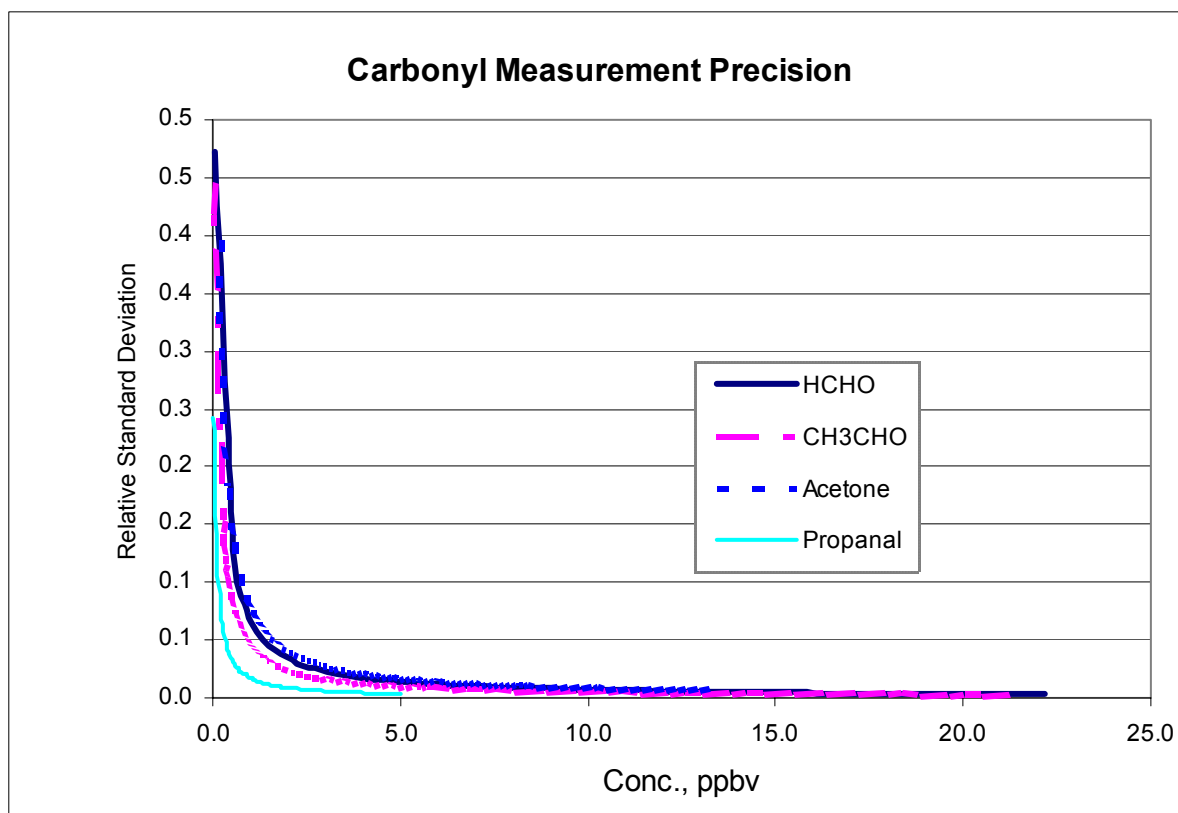


Figure 1: Measurement Precision for Formaldehyde, Acetaldehyde, Acetone, and Propanal.

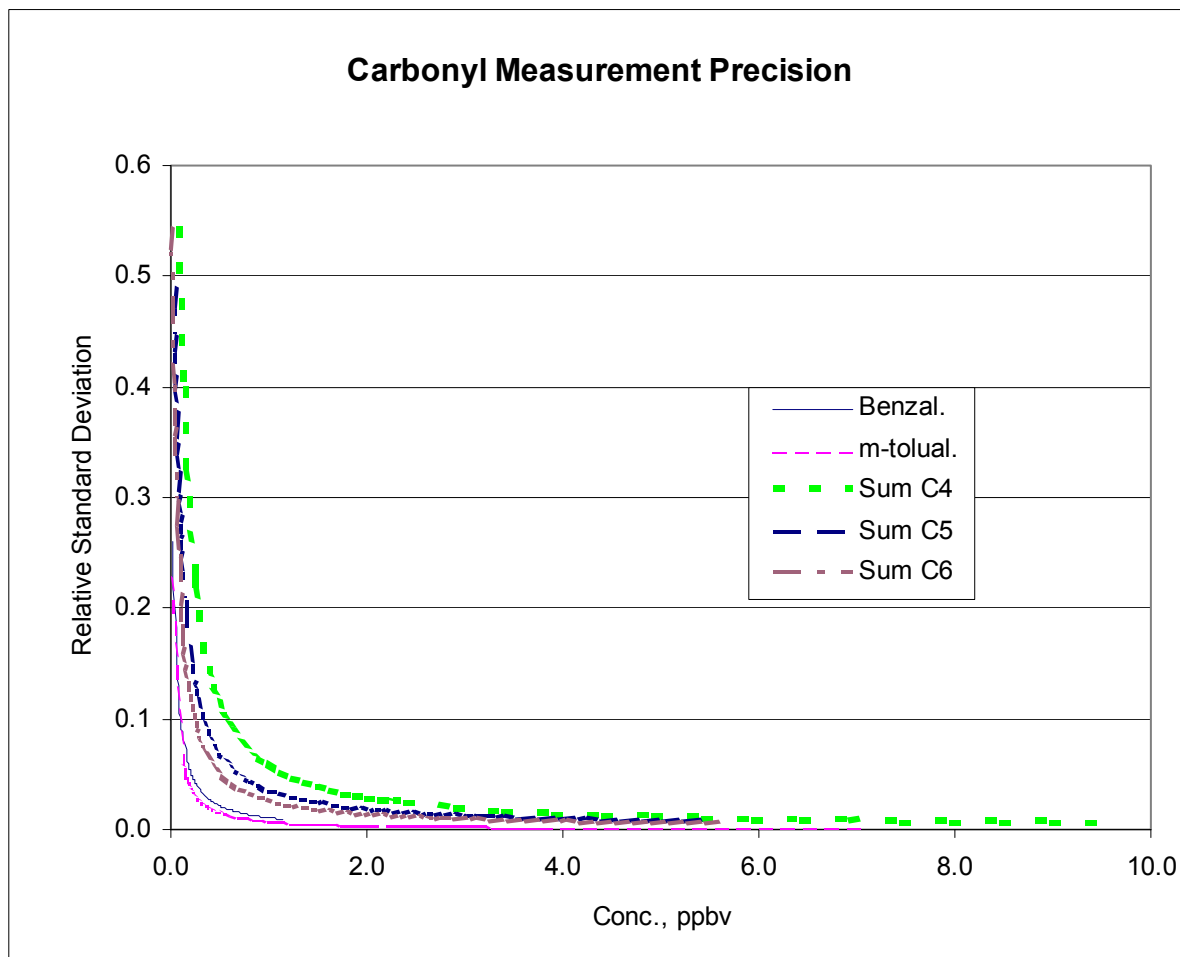


Figure 2: Measurement Precision for Benzaldehyde, m-Tolualdehyde, Total C4, Total C5 and Total C6 Carbonyl Compounds.

Table 2: Summary of Sites with Missing Samples or Problems During the CCOS Study.

Site	IOP	Sampling Period				Remarks
		00:00	06:00	13:00	17:00	
Angiola	21-Sep-00	No sample	No sample			Timer not activated for first two periods.
Arvine	14-Aug-00					Obstructed sampling line; flow rate uncertain.
	14-Sep-00					Obstructed sampling line; flow rate uncertain.
	17-Sep-00					Obstructed sampling line; flow rate uncertain.
	18-Sep-00					Obstructed sampling line; flow rate uncertain.
	19-Sep-00					Obstructed sampling line; flow rate uncertain.
	20-Sep-00					Obstructed sampling line; flow rate uncertain.
	21-Sep-00					Obstructed sampling line; flow rate uncertain.
Bodega Bay	14-Sep-00	Unexposed				Time slot not activated
	17-Sep-00	Unexposed				Time slot not activated
	18-Sep-00	Unexposed				Time slot not activated
Granite Bay	14-Aug-00	No sample	No sample	No sample	No sample	Pump was switched off after audit.
Pacheco Pass	14-Aug-00	No sample	No sample			Operator error, timer not activated.
	19-Sep-00				Suspect	No clear indication of problem.
Parlier	30-Jul-00				No sample	Operator error, time slot not activated.
	31-Jul-00				No sample	Operator error, time slot not activated.
	1-Aug-00				No sample	Operator error, time slot not activated.
	21-Sep-00	No sample	No sample			Operator error, time slot not activated.
Patterson Pass	14-Aug-00	Started early	Started early	Started early	Started early	Clock set 1 hr ahead accidentally by operator.
San Andreas	14-Sep-00				Suspect	Faulty cartridge connection.
	18-Sep-00			No sample		Audit interrupted sampling.
	19-Sep-00			Suspect		Faulty cartridge connection? Sampled room air?
San Leandro	23-Jul-00		No sample	No sample	No sample	Operator cleared the program accidentally.
	24-Jul-00		No sample			Program not correctly re-installed.
Sutter Buttes	1-Aug-00	No sample	No sample	No sample	No sample	Operator did not activate timer.

Note: IOP days were July 23-24, July 30-31, August 1, August 14, September 14*, September 17-21. Only Angiola, Arvin, Bodega Bay, Parlier, and San Jose 4th Street operated on September 14 IOP.

Arvin started sampling from August 14.

4. REFERENCES

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